




DECLARATION

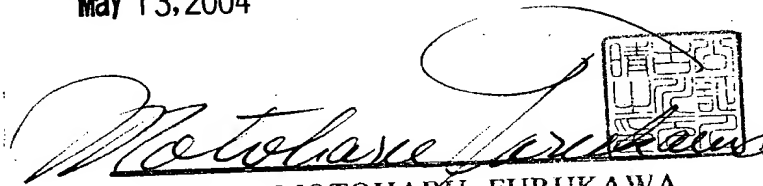
I, Japanese Patent Attorney Yoshitaka OSHIDA, having my office at GINZA BUILDING 3-12, 3-CHOME, GINZA CHUO-KU, TOKYO, JAPAN, do solemnly and sincerely declare:

1. That I am well acquainted with the Japanese and English languages, and
2. That the attached document: Specification
is a true translation into the English language.

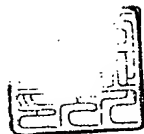
And I make this solemn declaration conscientiously believing the same to be true and correct.


Yoshitaka OSHIDA

Affirmed before me
May 13, 2004


Notary : MOTOHARU FURUKAWA
5-2-1 Kojimachi, Chiyoda-ku, Tokyo Japan.
Tokyo Legal Affairs Bureau





JAPAN PATENT OFFICE

This is to certify that the annexed is a true copy of the following application as filed with this office.

Date of Application : March 10, 1999

Application Number: JP1999-063093

Applicant(s): NEOMAX CO.,LTD.

May 7, 2004

Commissioner, Japan Patent Office: Yasuo IMAI

Certificate No. 2004-3038404



証

嘱託人 弁理士 押田良隆 は、添付書類の署名が自己のものに
相違ない旨、本公証人に対し自認した。

よって、これを認証する。

平成16年 5 月 13 日、本公証人役場において

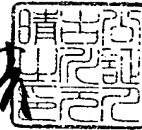
東京都千代田区麹町5丁目2番地1

東京法務局所属

公証人

Notary

押田 久 (印)



MOTOHARU FURUKAWA

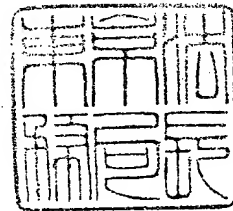
証 明

上記署名は、東京法務局所属公証人の署名に相違ないものであり、かつ、その押印は、
真実のものであることを証明する。

平成16年 5 月 13 日

東京法務局長

石井 政治



APOSTILLE

(Convention de La Haye du 5 octobre 1961)

1. Country: JAPAN

This public document

2. has been signed by MOTOHARU FURUKAWA

3. acting in the capacity of Notary of the Tokyo Legal Affairs Bureau

4. bears the seal/stamp of

Certified

5. at Tokyo

6. 13 th May , 2004

7. by the Ministry of Foreign Affairs

8. 04- NO 018829

9. Seal/stamp:

10. Signature

Shinichi HAGIWARA

For the Minister for Foreign Affairs

(Title of document) Patent Application
 (File No.) 30P99005
 (Filing date) MARCH 10, 1999
 To: Director-General of Patent Office : Takeshi ISAYAMA
 (International Patent Classification): HO1L 35/14
 C10B 33/06
 (Inventor):
 (Address or Residence) c/o, SUMITOMO SPECIAL METALS CO.,
 LTD. , of 2-15-17, Egawa, Shimamoto-cho,
 Mishima-Gun, Oosaka Prefecture
 (Name) Nobuhiro SADATOMI
 (Address or Residence) c/o, SUMITOMO SPECIAL METALS CO.,
 LTD. , of 2-15-17, Egawa, Shimamoto-cho,
 Mishima-Gun, Oosaka Prefecture
 (Name) Osamu YAMASHITA
 (Applicant)
 (Identification Number) 000183417
 (Address or Residence) 7-19 kitahama , 4-chome, Chuo-ku,
 Osaka-shi, OSAKA
 (Name or Title) SUMITOMO SPECIAL METALS CO.,LTD.
 (Proxy)
 (Identification No.) 100073900
 (Address or Residence) Ginza Bldg., 3-12,3-chome, Ginza
 Chuo-ku, Tokyo, JAPAN
 (Patent Attorney)
 (Name or Title) Yoshihisa OSHIDA
 (Telephone No.) 03-3561-0274
 (FEE)
 (Number of Note) 055918
 (Amount) 21000
 (List of Filing Documents)
 (Title) Specification 1
 (Title) Drawings 1
 (Title) Abstract 1
 (Number of General Power of Attorney) 9710264
 (Proof) yes

【Name of Document】 Specification

【Title of Invention】 METHOD FOR MANUFACTURING
THERMOELECTRIC CONVERSION MATERIAL

【What is claimed is】

【Claim 1】 A method of manufacturing a thermoelectric conversion material, including the steps of coating a silicon powder with an added element to make a silicon a p-type and/or n-type semiconductor by a vapor phase growth method or discharge plasma treatment such that the silicon powder contains added elements to make a p-type or n-type semiconductor in an amount 0.001 to 20 at%, either singly or in combination, and sintering to obtain a sintered body having a structure in which said added element-rich phase is formed at the grain boundary of a silicon-rich phase composed mainly of silicon.

【Claim 2】 The method of manufacturing a thermoelectric conversion material according to claim 1, wherein a silicon powder itself contains an added element to make a p-type or n-type semiconductor.

【Claim 3】 A method of manufacturing a thermoelectric conversion material, including the steps of coating a silicon powder containing in silicon an added element to make a p-type or n-type semiconductor with a silicon or an added element to make a p-type or n-type semiconductor by a plasma treatment using a gas containing a silicon or an added element to make a p-type or n-type

semiconductor such that the silicon powder contains the added elements to make a p-type or n-type semiconductor in an amount of 0.001 to 20 at%, either singly or in combination and sintering to obtain a sintered body having a structure in which said added element-rich phase is formed at the grain boundary of a silicon-rich phase composed mainly of silicon.

【 Claim 4 】 A method of manufacturing a thermoelectric conversion material, including the steps of embedding a silicon or an added element to make a p-type or n-type semiconductor into a silicon powder or a silicon powder containing an added element to make a p-type or n-type semiconductor in silicon by a mechanofusion treatment such that a silicon powder contains the added elements to make a p-type or n-type semiconductor in an amount of 0.001 to 20 at%, either singly or in combination, and sintering to obtain a structure in which said added element-rich phase is formed at the grain boundary of a silicon-rich phase composed mainly of silicon.

【 Detailed Description of the Invention 】

【 0001 】

【 Technical Field of the Invention 】

This invention relates to a novel thermoelectric conversion material composed of a sintered body, in which silicon is made to contain various types of added elements at an amount of 20 at% or less, and more particularly

relates to a polycrystal silicon-based thermoelectric conversion material composed of a sintered body, characterized in that by making a vapor phase growth film formation for a silicon powder, plasma treating by GH_4 gas to obtain a silicon-based material powder of the required composition, sintering and making a structure in which an added element-rich phase is dispersively formed at the grain boundary of a silicon-rich phase, a Seebeck coefficient becomes extremely large and a thermal conductivity small, allowing the thermoelectric conversion efficiency to be raised dramatically, and silicon, which is an abundant resource, is chiefly contained and environmental pollution is extremely little.

【0002】

【Background Art】

Thermoelectric conversion elements are devices that are expected to see practical use because of their efficient utilization of the high levels of thermal energy required in recent industrial fields. An extremely broad range of applications have been investigated, such as a system for converting waste heat into electrical energy, small, portable electric generators for easily obtaining electricity outdoors, flame sensors for gas equipment, and so forth.

【0003】

This conversion efficiency from thermal energy to

electrical energy is a function of the Figure of merit ZT , and rises in proportion to ZT . This Figure of merit ZT is expressed by Formula 1.

$$ZT = \frac{\alpha^2 \sigma T}{\kappa} \quad \text{Formula 1}$$

Here, α is the Seebeck coefficient of the thermoelectric material, σ is the electrical conductivity, κ is the thermal conductivity, and T is the absolute temperature expressed as the average value for the thermoelectric element on the high temperature side (T_H) and the low temperature side (T_L).

【0004】

Silicides such as FeSi_2 and SiGe , which are thermoelectric conversion materials that have been known up to now, are abundant natural resources, but the former has a Figure of merit ZT of 0.2 or less, its conversion efficiency is low, and its usable temperature range is extremely narrow, while no decrease in thermal conductivity is seen with the latter unless the germanium content is about 20 to 30 at%, and germanium is a scarce resource. Also, silicon and germanium have a state in which there is a broad liquidus and solidus for complete solid solution, and it is difficult to produce a uniform composition with melting or ZL (zone leveling), to impede industrial application. For these reasons, the above-mentioned materials have not found widespread use.

【0005】

The thermoelectric materials with the highest Figure of merit at the present time are IrSb₃ having a skutterudite-type crystal structure, and BiTe, PbTe, and other such chalcogen compounds, which are known to provide highly efficient thermoelectric conversion capability, but from the standpoint of protecting the global environment, the use of these heavy metal elements is expected to be restricted in the future.

【0006】

【Problems to be solved by the Invention】

Silicon, meanwhile, has a high Seebeck coefficient, but has extremely high thermal conductivity, and is therefore not considered suitable as a high efficiency thermoelectric material, and research into the thermoelectric characteristics thereof has been limited to silicon with a carrier concentration of $10^{18}(\text{Mm}^3)$ or less.

【0007】

The inventors discovered that doping silicon single piece with various elements, such as doping silicon with both a trace amount of a Group III element or Group V element and a small amount of germanium, makes it possible to lower thermal conductivity, and the Seebeck coefficient will be equivalent to or better than that of conventional Si-Ge and Fe-Si compounds, or will be extremely high at a given carrier concentration. They also discovered that this material exhibits a good Figure of merit as a

thermoelectric conversion material and improve performance, without losing the fundamental advantages afforded by silicon single piece.

【0008】

The inventors also produced p- and n-type semiconductors by doping a silicon with various elements, and examined the relationship of the doping amount to the thermoelectric characteristics, and as a result found that up to an added amount (that is, a carrier concentration) of $10^{18}(\text{M}/\text{m}^3)$, the Seebeck coefficient decreases in inverse proportion to the carrier concentration, but has a maximum value from 10^{18} to $10^{19}(\text{M}/\text{m}^3)$.

【0009】

It is an object of the present invention to further lower thermal conductivity or further enhance the Seebeck coefficient and thereby improve performance, without sacrificing the high Seebeck coefficient and electrical conductivity had by this novel silicon-based thermoelectric conversion material discovered by the inventors.

【0010】

【Means to solve the Problems】

The inventors diligently examined the mechanism by which a high Seebeck coefficient is obtained with a silicon-based thermoelectric conversion material doped with various added elements, whereupon they learned that this novel silicon-based material has a structure in which at the

grain boundary of a silicon-rich phase containing mainly silicon, an added element-rich phase is formed.

【0011】

The inventors also investigated a crystal structure, and they discovered that since the added element cohesion occurs at the crystal grain boundary and the conduction of carriers can be increased, a high Seebeck coefficient is obtained in the silicon-rich phase within the crystal grain.

【0012】

In view of this, the inventors tried controlling the crystal structure aside from composition as a method for keeping the Seebeck coefficient high and lowering the thermal conductivity, whereupon they found that by pulverizing the raw material obtained by ordinary cooling or quenching in melting and solidification, forming and sintering the pulverized powder, for example, with hot pressing or plasma sintering, the crystal grain diameter can be made fine 1 to 50 μm , and a material having a structure in which a silicon-rich phase and added element-rich phase are dispersed at the required arrangement in the material and a high Figure of merit will be obtained.

【0013】

Further, as a method of obtaining a silicon-based powder for sintering, the inventors found that it is possible to obtain a thermoelectric conversion material composed of a sintered body having a structure in which, by

coating with an added element a silicon powder or a silicon powder containing an added element in silicon by a vapor phase growth method such as vapor deposition, sputtering, or CVD, or a discharge plasma treatment, or coating the added element by plasma treatment using a gas containing an added element, embedding an added element by mechanofusion treatment such that a silicon powder contains an added element to make a p-type or n-type semiconductor in an amount of 0.001 to 20 at%, either singly or in combination and sintering it, said added element-rich phase is formed at the grain boundary of a silicon-rich phase composed mainly of silicon.

【0014】

【Mode of Working of the Invention】

The structure in which the above-mentioned added element-rich phase is formed at the boundary of the silicon-rich phase composed of mainly silicon, which is a characteristic feature of the thermoelectric conversion material of the present invention, will now be described. First, $\text{Si}_{1-x}\text{Ge}_x$ melts (at%) were produced by arc melting, with various added amounts of germanium (4N) into high purity silicon (10N), were quenched at a cooling rate of 50 to 200K/sec after melting to produce sample substrates. The crystal structure was observed by EPMA. As shown in Figure 1A, when $x = 0.03$, the black parts in the photographs are the silicon-rich phase, which is virtually

all silicon, although a trace amount of added element is included, and the white parts are the added element germanium rich-phase, and it can be seen that in this structure the germanium-rich phase is formed or dispersed at the grain boundary of the silicon-rich phase.

【0015】

Also, a trace amount of phosphorus was added to the above-mentioned $\text{Si}_{1-x}\text{Ge}_x$ melts, but when just the phosphorus was observed, the EPMA photographs were as shown in Figure 1B, with the white parts indicating places where the doped phosphorus is present, and it can be seen that in this structure the phosphorus is segregated in the same locations where the germanium-rich phase in Figure 1A as mentioned above was formed at the grain boundary of the silicon-rich phase.

【0016】

In other words, the structure of the thermoelectric conversion material of the present invention, as shown by the schematic diagram in Figure 2, is a structure in which are formed a silicon-rich phase consisting of silicon alone or almost entirely of silicon but including a trace amount of added element, and an added element-rich phase in which an added element is segregated at the grain boundary of this silicon-rich phase.

【0017】

A sample substrate was produced by cooling at a rate

of 50K/sec after melting, the substrate was then pulverized into a powder with an average particle size of $30\text{ }\mu\text{m}$, a $\text{Si}_{1-x}\text{Ge}_x$ (at%) powder coated with an added element was produced by discharge plasma treatment, and this powder was sintered at 1250 to 1350°C. The crystal structure of the obtained sample was observed by EPMA, which revealed that melting and solidification produced the same structure as in Figure 1 and that the size of the silicon-rich phase was a relatively small 10 to $100\text{ }\mu\text{m}$.

【0018】

The relationship between carrier concentration of an n-type and p-type silicon and the state of crystal grain boundary deposition of an added element of phosphorus or boron instead of germanium was examined, which confirmed that the correlation of the carrier concentration and the doping amount increased agreeably. Because of the structure in which the added element-rich phase was formed at the grain boundary of the silicon-rich phase, the added element was clumped at the crystal grain boundary, the electrical conductivity resulting from carriers was high, a high Seebeck coefficient was obtained in the silicon-rich phase within the crystal grains.

【0019】

Furthermore, it was confirmed that the thermal conductivity of this silicon-based thermoelectric conversion material decreases as the carrier concentration

is increased. This is believed to be because κ_{ph} was decreased by local phonon scattering of impurities resulting from the added element in the crystals.

【0020】

A structure in which an added element-rich phase of germanium or the like is dispersively formed at the grain boundary of a silicon-rich phase, which is a characteristic of a silicon-based thermoelectric conversion material composed of a sintered body, is formed through the segregation of the added element within the raw material powder particles or on the surface during sintering. It is also effective for the sintering powder itself to have the same crystal structure. This can be obtained by controlling the cooling rate after casting, the crystal grain size is kept relatively small by quenching, segregation of a suitable added element other than silicon occurs at the crystal grain boundary, and this results in a material powder exhibiting a high Seebeck coefficient despite the high electrical conductivity. Furthermore, sintering using this powder causes the segregation of the added element during sintering to occur more readily and effectively, and a sintered silicon-based thermoelectric conversion material that exhibits a high Seebeck coefficient is obtained.

【0021】

In the present invention, even if the raw material

has little of the above-mentioned segregation of a suitable added element other than silicon at the crystal grain boundary, the required segregation will occur during sintering and the targeted structure can be obtained, so there are no particular restrictions on the cooling rate of the silicon-based molten material.

【0022】

Cooling methods to obtain a silicon or silicon-based powder in the present invention include cooling the ingot just as it is, and cooling while pulling, such as method in which a known CZ or FZ method for obtaining monocrystalline silicon is utilized and pulling and cooling are performed under conditions that allow polycrystalline silicon to be obtained. Manufacture by ZL method is also possible.

【0023】

Other methods may also be employed, such as a method in which a thin sheet is fabricated by casting and cooling a silicon-based molten material in a shallow plate, or utilizing a roll cooling method such as a known melt quenching method to control the cooling rate so that a thin sheet of the required thickness will be obtained.

【0024】

Further, to obtain a silicon or a silicon-based powder, it is possible to manufacture ribbons by a roll cooling method such as melt quenching and to powder, or to obtain the powders directly with a spraying method such as

gas atomization, allowing for a fine crystal grain size of 1 to 50 μm and making it possible to lower the thermal conductivity.

【0025】

According to the present invention, a silicon alone or a silicon-based melting raw material of the required composition is melt by an arc melting or a high frequency melting method for casting, insufficient added elements are adhered on the surface of the silicon or the silicon-based powder particle of the required particle size obtained by pulverizing cast ingots and thin sheets, and sintered to obtain a structure wherein an added element-rich phase is dispersively formed at the grain boundary of a silicon-rich phase of the required composition as shown in Fig. 2.

【0026】

As a method of coating with added elements on the surface of silicon powder or silicon powder containing added elements in silicon, any growth, film formation, binding, or adhesive means such as a known vapor phase growth method like vapor deposition, sputtering, CVD, discharge plasma treatment, and plasma treatment using a gas containing added elements can be employed, and further a method of embedding added elements on the surface of silicon powder by mechanofusion treatment can be employed.

【0027】

The phrase "coating with an added element" as used

in the present invention encompasses everything from forming a complete film on the silicon particle surface to merely causing added element particles to adhere to the silicon particle surface. In other words, the added element particles need not completely cover the silicon particle surface, and may instead just adhere up to the time of the sintering treatment. Also, as will be discussed below, any element can be added as the added element, so a variety of cases are conceivable, including those in which any means can be selected and those in which the means is limited by the type of element in question. In addition, the treatment conditions for the selected means will vary considerably with the combination of elements when two or more are used, so the above-mentioned means and conditions must be appropriately selected according to the targeted composition.

【0028】

For instance, the example shown in Figure 3A is one in which an added element has been bound to the particle surface of a silicon powder adjusted to a specific particle size by pulverizing an ingot or thin sheet by said method, or a silicon powder obtained directly by spray method. The binding may be accomplished by any means, such as growth or film formation as discussed below, and the binding amount is suitably selected so as to achieve the targeted composition after sintering. The same treatment can be performed on

silicon-based particles in which the silicon powder itself contains the required added element. The structure in which an added element-rich phase is dispersively formed at the grain boundary of a silicon-rich phase shown in Figure 2 can be obtained by sintering a silicon powder composed of silicon particles in which the required added element is bound to the surface.

【0029】

The example shown in Figure 3B is one in which the added element is imbedded in the silicon particle surface by mechanofusion treatment so that the silicon particles are silicon-rich particles, and the structure in which an added element-rich phase is dispersively formed at the grain boundary of a silicon-rich phase shown in Figure 2 can be obtained by sintering a silicon-rich powder composed of silicon-rich particles in which the required added element is imbedded in the surface.

【0030】

Any sintering method can be used in the present invention as long as it allows for firing at about 1250 to 1350°C, which is close to the melting point of silicon. An ordinary firing method in which sintering is performed after compression molding, or a known sintering means such as hot pressing or discharge plasma sintering in which sintering is performed during compression molding, can be selected as deemed appropriate. The preferred conditions

should be appropriately selected according to the selected sintering means such that the sintering time is maintained at 0.5 hour or longer, the temperature is 1200 to 1350°C, and the sintering is performed in a vacuum or an inert gas.

【0031】

A thermoelectric conversion material according to the present invention is a highly efficient silicon-based thermoelectric conversion material of a p-type and n-type semiconductor which lowers the electric resistance, improves the Seebeck coefficient and improves dramatically Figure of merit without losing the fundamental advantages afforded by silicon single piece by making a structure added with various impurities into the polycrystalline silicon semiconductor having a diamond-like crystal structure by sintering and adjusting the carrier concentration.

【0032】

When the applications of a thermoelectric conversion material are considered, emphasis must be placed on one of the characteristics, such as the Seebeck coefficient, electrical conductivity, or thermal conductivity depending on the conditions which vary with the application, such as the heat source, where and how the material is used, and the size of the current and voltage to be handled, but the thermoelectric conversion material of the present invention allows the carrier concentration to be determined by means of the added amount of the selected added element.

【0033】

For example, when one or more elements from the above-mentioned added elements α are contained in an amount of 0.001 to 0.5 at%, a p-type semiconductor with a carrier concentration of 10^{17} to 10^{20} (M/m³) will be obtained, and when added elements α are contained in an amount of 0.5 to 5.0 at%, a p-type semiconductor with a carrier concentration of 10^{19} to 10^{21} (M/m³) will be obtained.

【0034】

Similarly, when one or more elements from the above-mentioned added elements β are contained in an amount of 0.001 to 0.5 at%, an n-type semiconductor with a carrier concentration of 10^{17} to 10^{20} (M/m³) will be obtained, and when added elements β are contained in an amount of 0.5 to 10 at%, an n-type semiconductor with a carrier concentration of 10^{19} to 10^{21} (M/m³) will be obtained.

【0035】

When the above-mentioned added elements α or added elements β are contained in an amount of 0.5 to 5.0 at% so that the carrier concentration is 10^{19} to 10^{21} (M/m³), a highly efficient thermoelectric conversion element is obtained, and the thermoelectric conversion efficiency is excellent, but the thermal conductivity thereof is about 50 to 150 W/m · K at room temperature, and if the thermal conductivity could be decreased, there would be a further

improvement in the Figure of merit ZT.

【0036】

Generally, the thermal conductivity of solids is given as a sum of the conduction due to phonon and the conduction due to carrier. In case of thermoelectric conversion material of a silicon-based semiconductor, since the carrier concentration is small, the conduction due to phonon is dominant. Therefore, to decrease the thermal conductivity, it is necessary to make the absorption or scattering of phonon large. In order to make the absorption or scattering of phonon large, it is effective to disturb the regularity of the crystal structure, and the crystal grain size.

【0037】

It is possible to disturb the crystal structure without changing the carrier concentration in silicon by adding at least one Group III element and at least one Group V element to silicon and controlling the carrier concentration to a range of 10^{19} to 10^{21} (M/m³). The thermal conductivity can decrease 30 to 90%, to 150 W/m · K or less at room temperature, and a high efficiency thermoelectric conversion material can be obtained.

【0038】

Further, in the above constructed thermoelectric conversion material, a p-type semiconductor will be obtained if the Group III element is contained in an amount 0.

3 to 5 at% larger than the Group V element, and an n-type semiconductor will be obtained if the Group V element is contained in an amount 0.3 to 5 at% larger than the Group III element.

【0039】

The inventors also investigated whether a decrease in thermal conductivity could be achieved with something other than Group III elements and Group V elements, and found that the crystal structure can be disturbed without changing the carrier concentration in the silicon, the thermal conductivity can be brought below $150 \text{ W/m} \cdot \text{K}$ or less at room temperature, and a highly efficient thermoelectric conversion material can be obtained by adding a Group III-V compound semiconductor or a Group II-VI compound semiconductor to silicon, further adding at least one type of Group III element or Group V element and controlling the carrier concentration to a range of 10^{19} to $10^{21} (\text{M/m}^3)$.

【0040】

Furthermore, as a result of variously investigating other added elements to silicon, the inventors found that if the silicon contains the Group IV elements germanium, carbon, and tin in an amount of 0.1 to 5 at%, and some of the silicon elements are replaced with a Group IV element with a different atomic weight, there will be greater phonon scattering in the crystals and the thermal

conductivity of the semiconductor can be reduced 20 to 90%, to 150W/m · K or less at room temperature. Further, it is possible to obtain a thermoelectric conversion material wherein a p-type semiconductor is obtained if the Group III element is contained in an amount of 0.1 to 5.0 at% and furthermore a thermoelectric conversion material wherein an n-type semiconductor is obtained if the Group V element is contained in an amount of 0.1 to 10 at%.

【0041】

Other elements besides the above-mentioned Group III and V elements were examined to see if they could similarly be added to silicon in the thermoelectric conversion material of the present invention, whereupon it was confirmed that while there are no particular restrictions as long as a p- or n-type semiconductor will result, if elements whose ion radii are too different are used, almost all will precipitate in the grain boundary phase, so it is preferable to use an element whose ion radius is relatively close to that of silicon. It is confirmed that one or more elements of the following groups are particularly effective as added elements α to make a p-type semiconductor or as added elements β to make an n-type semiconductor.

【0042】

The added element α are each group consisting of added elements A (Be, Mg, Ca, Sr, Ba, Zn, Cd, Hg, B, Al, Ga,

In, Tl) and transition metal elements M_1 (Y, Mo, Zr). The added elements β are each group consisting of added elements B (N, P, As, Sb, Bi, O, S, Se, Te), transition metal elements M_2 (Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Nb, Ru, Rh, Pd, Ag, Hf, Ta, W, Re, Os, Ir, Pt, Au; where Fe accounts for 10 at% or less), and rare earth elements RE (La, Ce, Pr, Nd, Pm, Sm, Eu, Gd, Tb, Dy, Ho, Er, Yb, Lu).

【0043】

Further, if, in added elements α to make a p-type semiconductor and added elements β to make an n-type semiconductor, at least one type from each group is contained at an amount of 0.002 to 20 at% in total amounts, for example, if in order to obtain a p-type semiconductor the total amount of added elements α is contained only at the required amount to make a p-type semiconductor over that of added elements β , voluntary combinations of each group can be selected.

【0044】

【Examples】

Example 1

In order to produce mother particles of p-type and n-type silicon thermoelectric conversion semiconductors, high-purity silicon (10N) and added elements were compounded as shown in Table 1, after which this product was put in a graphite crucible and vacuum melted in a high-frequency melting furnace. After melting, the material was cast into

a mold with a thickness of 10 mm, and the ingots were ground and then pulverized to an average crystal grain size of 10 to 50 μ m in a stamp mill and a ball mill. The ball mill was a wet type and made use of a xylene solvent. The ground powder (mother particles) was put in a vacuum chamber at 10^{-3} Torr, and the surface of the particles was coated (film thickness: 10 to 100 μ m) with the elements shown in Table 1.

【0045】

The powder thus obtained was subjected to hot pressing in argon for 1 hour at 1325K and 1000kgf/cm² to obtain sinters. The sinter samples were cut to sizes of 5 × 5 × 15 mm, 10 × 10 × 2 mm, and 10 (outside diameter) × 2 mm, and the Seebeck coefficient, Hall coefficient (including carrier concentration and electrical conductivity), and thermal conductivity of each were measured. Table 2 shows the measured values at 1100K and the Figure of merit ($ZT = S^2T / \rho \kappa$).

【0046】

The temperature differential between the high and low temperature portions during temperature elevation was set to be about 6K, the thermoelectromotive force of the samples was measured with a digital mutimeter, and this value was divided by the temperature differencetial to find the Seebeck coefficient. The Hall coefficient was measured by AC method, and the electrical resistance was measured by

four-terminal method simultaneously with the carrier concentration. The thermal conductivity was measured by laser flash method.

【0047】

Example 2

In order to produce mother particles of p- and n-type silicon thermoelectric conversion semiconductors, high-purity silicon (10N) and added elements were compounded as shown in Table 3, after which this product was put in a graphite crucible and vacuum melted in a high-frequency melting furnace. After melting, the material was cast into a mold with a thickness of 10 mm to obtain sheet-form ingots. The ingots were then ground, and then finely pulverized to an average crystal grain size of 1 to 10 μm in a stamp mill and a jet mill. N_2 gas was used in the jet mill, and the pressure was 7kgf/mm².

【0048】

The powders (mother particles) thus obtained were put in a vacuum chamber and plasma-treated with SiH_4 gas or GeH_4 gas, and the powders were coated with boron, aluminum, gallium, phosphorus, arsenic, and antimony.

【0049】

The coated raw material powders were compression molded at a pressure of 2000kgf/cm² to sizes of 5 × 5 × 15 mm, 10 × 10 × 2 mm, and 10 (outside diameter) × 2 mm, and these products were sintered in a vacuum for 5

hours at 1325K. The Seebeck coefficient, Hall coefficient (including carrier concentration and electrical conductivity), and thermal conductivity of each of the sinters thus obtained were measured by the same methods as in Example 1. Table 4 shows the measured values at 1100K and the Figure of merit ($ZT = S^2T / \rho \kappa$).

【0050】

Example 3

In order to produce mother particles of p-type and n-type silicon thermoelectric conversion semiconductors, high-purity silicon (10N) and added elements were compounded as shown in Table 5, after which this product was put in a graphite crucible and vacuum melted in a high-frequency melting furnace. The melt was cast into a mold with a thickness of 10 mm to obtain sheet-form ingots. The ingots were ground and then finely pulverized to an average crystal grain size of 10 to 50 μ m in a stamp mill and a ball mill. The ball mill was a wet type and made use of a xylene solvent.

【0051】

High-purity silicon (10N) and added elements for producing daughter particles forming a coating around the silicon were compounded as shown in Table 5, after which the material was put in a graphite crucible and vacuum melted in a high-frequency melting furnace. The melt discharged through a nozzle with an inside diameter of 3 mm,

and the melts were quenched by blowing argon gas on them at 30kgf/cm³, resulting in an average particle diameter of 30 to 100 μ m. The obtained mother particles were coated with the daughter particles by mechanofusion such that the daughter particles were in a specific weight ratio.

【0052】

The coated raw material powders were sintered by discharge plasma in an argon atmosphere. The sintering conditions were 3 minutes at 1325K. The sample sinters were cut to sizes of 5 × 5 × 15 mm, 10 × 10 × 2 mm, and 10 (outside diameter) × 2 mm, and the Seebeck coefficient, Hall coefficient (including carrier concentration and electrical conductivity), and thermal conductivity of each were measured by the same methods as in Example 1. Table 6 shows the measured values at 1100K and the Figure of merit ($ZT = S^2T / \rho \kappa$).

【0053】

【Table 1】

No.	Composition of mother particles	Diameter of mother particles (μm)	Added element	Coating film thickness (nm)	Sintering temp. (K)	Sintering time (h)
1	Si	10	B	10	1325	1
2	Si	30	B	30	1325	1
3	Si	30	Al	50	1325	1
4	Si _{0.97} Ge _{0.03}	10	B	10	1325	1
5	Si _{0.97} Ge _{0.03}	30	B	30	1325	1
6	Si _{0.97} Ge _{0.03}	30	Ca	50	1325	1
7	Si	10	P	30	1325	1
8	Si	30	P	60	1325	1
9	Si	30	As	90	1325	1
10	Si _{0.97} Ge _{0.03}	10	P	30	1325	1
11	Si _{0.97} Ge _{0.03}	30	P	60	1325	1
12	Si _{0.97} Ge _{0.03}	30	Sb	90	1325	1

【0054】

【Table 2】

No.	Seebeck coefficient (mV/K)	Electrical resistivity $\times 10^{-5}$ ($\Omega \cdot m$)	Thermal conductivity (W/m · K)	Figure of merit (ZT)
1	0.267	1.31	29	0.21
2	0.259	1.28	31	0.19
3	0.234	1.41	35	0.12
4	0.271	1.35	9	0.66
5	0.269	1.33	11	0.54
6	0.289	1.42	10	0.65
7	-0.301	1.30	30	0.26
8	-0.299	1.28	32	0.24
9	-0.293	1.32	37	0.19
10	-0.309	1.34	9	0.87
11	-0.306	1.30	10	0.79
12	-0.329	1.48	10	0.80

【0055】

【Table 3】

No.	Composition of mother particles	Diameter of mother particles (μm)	Added element	Coating film thickness (nm)	Sintering temp. (K)	Sintering time (h)
21	Si	3	B	3	1325	5
22	Si	10	B	10	1325	5
23	Si	10	Al	15	1325	5
24	Si _{0.97} Ge _{0.03}	3	B	3	1325	5
25	Si _{0.97} Ge _{0.03}	10	B	10	1325	5
26	Si _{0.97} Ge _{0.03}	10	Ga	15	1325	5
27	Si	3	P	10	1325	5
28	Si	10	P	20	1325	5
29	Si	10	As	30	1325	5
30	Si _{0.97} Ge _{0.03}	3	P	10	1325	5
31	Si _{0.97} Ge _{0.03}	10	P	20	1325	5
32	Si _{0.97} Ge _{0.03}	10	Sb	30	1325	5

【0056】

【Table 4】

No.	Seebeck coefficient (mV/K)	Electrical resistivity $\times 10^{-5}$ ($\Omega \cdot m$)	Thermal conductivity (W/m · K)	Figure of merit (ZT)
21	0.271	1.39	24	0.24
22	0.262	1.31	29	0.20
23	0.237	1.46	31	0.14
24	0.273	1.40	8	0.73
25	0.271	1.37	10	0.59
26	0.291	1.46	10	0.64
27	-0.303	1.35	26	0.29
28	-0.301	1.32	29	0.26
29	-0.295	1.37	32	0.22
30	-0.311	1.39	8	0.96
31	-0.309	1.36	9	0.86
32	-0.331	1.52	9	0.88

【0057】

【Table 5】

No.	Composition of mother particles	Diameter of mother particles (μm)	Composition of daughter particles	Diameter of daughter particles (μm)	Sintering temp. (K)	Sintering time (sec)
41	Si	10	B	1	1325	180
42	Si	30	B	3	1325	180
43	Si	30	Al	3	1325	180
44	Si	10	Ge _{0.9} B _{0.1}	1	1325	180
45	Si	30	Ge _{0.9} B _{0.1}	3	1325	180
46	Si	30	Ge _{0.9} Ga _{0.1}	3	1325	180
47	Si	10	P	1	1325	180
48	Si	30	P	3	1325	180
49	Si	30	As	3	1325	180
50	Si	10	Ge _{0.8} P _{0.2}	1	1325	180
51	Si	30	Ge _{0.8} P _{0.2}	3	1325	180
52	Si	30	Ge _{0.8} Sb _{0.2}	3	1325	180

【0058】

【Table 6】

No.	Seebeck coefficient (mV/K)	Electrical resistivity $\times 10^{-5}$ ($\Omega \cdot m$)	Thermal conductivity (W/m · K)	Figure of merit (ZT)
41	0.273	1.40	28	0.21
42	0.265	1.33	31	0.19
43	0.240	1.49	33	0.13
44	0.275	1.42	9	0.65
45	0.274	1.39	10	0.59
46	0.294	1.48	10	0.64
47	-0.304	1.37	28	0.27
48	-0.302	1.35	30	0.25
49	-0.297	1.39	33	0.21
50	-0.314	1.41	9	0.85
51	-0.312	1.39	10	0.77
52	-0.333	1.54	10	0.79

【0059】

【Effects of the Invention】

Silicon, the main component of the thermoelectric conversion material of the present invention, is an outstanding material in terms of protecting the global environment and conserving the earth's resources, and also affords excellent safety. Furthermore, it is light (has a low specific gravity), which makes it very favorable for thermoelectric conversion elements used in automobiles. Bulk silicon also has good corrosion resistance, which is an advantage in that no surface treatment or the like is needed.

【0060】

Because it makes use of silicon as its main component, the thermoelectric conversion material of the present invention is less expensive than Si-Ge-based materials containing large quantities of costly germanium, and provides a higher Figure of merit than Fe-Si-based materials. Furthermore, the silicon used in the present invention is much lower in purity than that used in semiconductor devices, so the raw material is available at relatively low cost, the result of which is a thermoelectric conversion material with good productivity, stable quality, and low cost.

【0061】

The thermoelectric conversion material of the

present invention takes full advantage of the characteristics of silicon, namely, its low electrical resistance and large Seebeck coefficient despite having a large carrier concentration, and also greatly ameliorates its drawback of high thermal conductivity, and is therefore an effective way to obtain a material with a high Figure of merit. Another advantage is that the properties can be controlled by means of the type and amount of added elements.

【Brief Explanation of Drawings】

【Fig. 1】

Fig. 1 is a photograph taken by EPMA of the crystal structure of the thermoelectric conversion material of the present invention, where A shows the segregation of a germanium added element, and B shows the segregation of a phosphorus added element.

【Fig. 2】

Fig. 2 is a schematic diagram illustrating the crystal structure of the thermoelectric conversion material of the present invention.

【Fig. 3】

Fig. 3 is a schematic diagram illustrating the state of silicon particles of the thermoelectric conversion material powder of the present invention, where A shows the added element on the surface, and B shows the added element embedded.

【Name of Document】 Summary

【Summary】

【Objects】 It is to improve performance or further enhance the Seebeck coefficient by having a high Seebeck coefficient provided with a novel silicon-based thermoelectric conversion material in which various added elements are contained in silicon at an amount of 20 at% or less, and by decreasing further the thermal conductivity without decreasing an electrical conductivity of the material.

【Means for solving】 By making a vapor phase growth film formation for a silicon powder, obtaining a silicon-based material powder of the required composition by plasma treatment with GeH_4 gas and sintering this, and making a structure wherein an added element-rich phase is dispersed in the grain boundary of a silicon-rich phase, it is possible to obtain an extremely large Seebeck coefficient and low thermal conductivity, allowing the thermoelectric conversion rate to be raised dramatically, and to obtain a polycrystal silicon-based thermoelectric conversion material composed of a sintered body, wherein a silicon which is an abundant resource is a main component and an environmental pollution is extremely little.

【Selected Figure】 Fig. 2

日 本 国 特 許 庁
JAPAN PATENT OFFICE

別紙添付の書類に記載されている事項は下記の出願書類に記載されて
いる事項と同一であることを証明する。

This is to certify that the annexed is a true copy of the following application as filed
with this Office.

出 願 年 月 日 1 9 9 9 年 3 月 1 0 日
Date of Application:

出 願 番 号 平成 1 1 年 特 許 願 第 0 6 3 0 9 3 号
Application Number:

ST. 10/C]: [J P 1 9 9 9 - 0 6 3 0 9 3]

願 人 株式会社 NEOMAX
Applicant(s):

2 0 0 4 年 5 月 7 日

特許庁長官
Commissioner,
Japan Patent Office

今 井 康 夫

